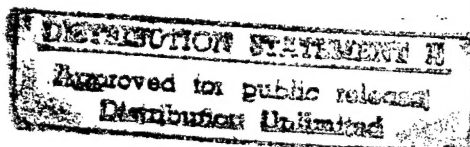AECD-4101

UNITED STATES ATOMIC ENERGY COMMISSION

ELECTROLYTIC REDUCTION OF URANYL AND FERRIC SULFATE SOLUTIONS

By
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Topical Report

ELECTROLYTIC REDUCTION OF URANYL AND

FERRIC SULFATE SOLUTIONS

By

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Approved for A. M. Gaudin, Director

By _Albert W. Owens_
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May 12, 1950

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The efficiency of reduction of uranyl and ferric ions was studied, both separately and together. Current efficiencies were studied in relation to concentration, current density, and the presence or absence of mechanical agitation of the electrolyte.

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I. INTRODUCTION

Some studies on the efficiency of electrolytic reduction of uranyl uranium and ferric iron, singly and in combination, in pure solutions have been carried out at this laboratory. Topical Report A-35* by E. Michal describes the earliest work carried out at this project and GML-13* describes similar tests carried out at another site. This report will describe another series of tests investigating these reactions.

II. SUMMARY

The current efficiency of reduction of uranyl ion decreases with increasing pH between the values of pH 0.1 and pH 2.6. Ferric ion reduction shows no appreciable change in this same range.

The current efficiency for reduction of both ferric and uranyl ions varies almost inversely with increasing current density in the range of 0.5 to 9 amperes per square foot.

Increasing the concentration of uranyl ion by a factor of 50 increases the current efficiency 60 fold. Increasing the ferric ion concentration by a factor of 50 increases the current efficiency 10 fold.

Mechanical agitation is helpful; the current efficiency doubles with mechanical agitation of 150 r.p.m. and more than doubles at 500 r.p.m.

Ferric ion at an initial concentration of 2 grams per liter is reduced at a rate directly proportional to the concentration; uranyl ion at 0.1 gram per liter is reduced more slowly. The reduction of ferric ion is enhanced by the presence of uranyl ion.

III. EXPERIMENTAL WORK

A. Materials and Methods

The reduction tests were carried out in a diaphragm cell using a cylindrical sheet lead cathode, 0.19 square feet in area, fitted snugly inside a 600 ml beaker, a cylindrical Cenco No. 79161 ceramic diaphragm inside the cathode, and a graphite anode inside the diaphragm. The cathode compartment contained 200 ml of the solution being reduced; the anode compartment was filled with 1 per cent sulfuric acid. Except for the tests run with varying concentrations of uranium and iron, and those run on solutions containing both uranium and iron, the concentration of uranium in the cathode compartment was 0.0975 gram per liter and that of the iron was 2.16 grams per liter. Six-volt storage batteries, or a battery charger, connected across a potentiometer provided the current. The percentage reduction was determined after each test by titration with permanganate*.

B. Experimental Results

The effect of several variables on the efficiency of reduction was investigated.

1. pH. Figure 1 shows the effect of the initial pH of the solution on the reduction of ferric and uranyl ions. The efficiency of reduction of ferric ion remained constant at 44 per cent between pH 0.1 and pH 2.0. The efficiency of uranyl ion reduction fell linearly from a value of 2.3 per cent at pH 0.1 to 0.7 per cent at pH 2.6.

2. Current Density. The effect of varying the current density is shown in Figure 2. The current efficiency varies almost inversely with current density for both ferric and uranyl ions. The amp-sec or coulomb quantity was held constant in each series of tests, being 860 for ferric reduction and 420 for uranyl reduction.

3. Concentration. The efficiency as a function of concentration for uranyl and ferric ions is shown in Table 1. It is seen that the current efficiencies increase rapidly with increasing concentrations of the two ions.

Table 1. Efficiency of Reduction of Uranyl and Ferric Ions as a Function of Concentration

Amp-Sec	Uranyl Ion : Initial pH 0.75			Ferric Ion : Initial pH 1.35		
	Conc g/l	Per Cent Reduction	Per Cent Current Efficiency	Conc g/l	Per Cent Reduction	Per Cent Current Efficiency
420	0.098	30	1.1	0.045	44	1.6
640	0.98	57	14	0.5	31	8.2
860	4.7	75	66	2.2	20	17

These tests confirm the results shown in Figure 2 in which the difference in concentration accounts for the difference in current efficiency.

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* Details of the stock solution production and titration procedures are given in Appendix A.
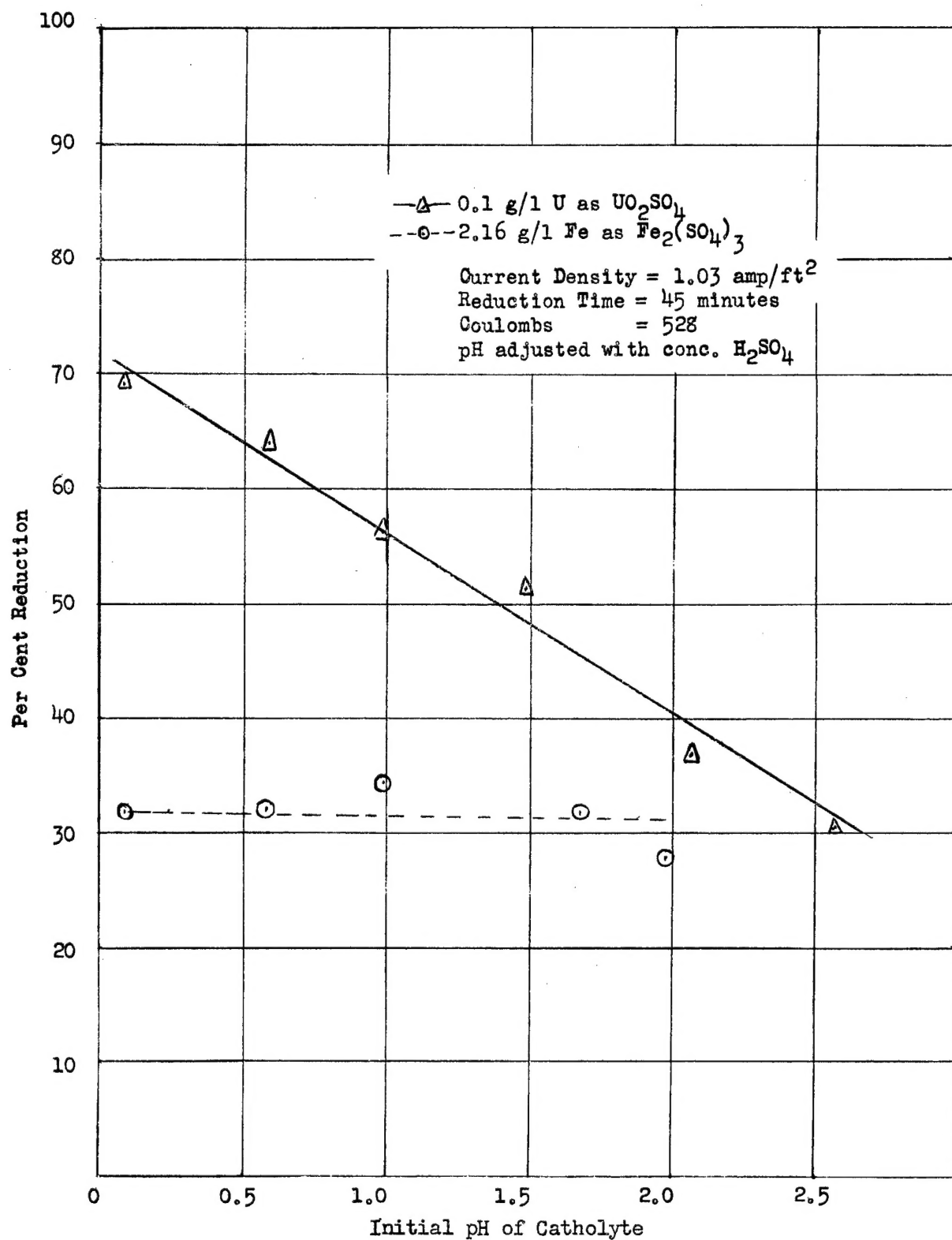
Figure 1. Effect of Initial pH of Catholyte on Reduction of
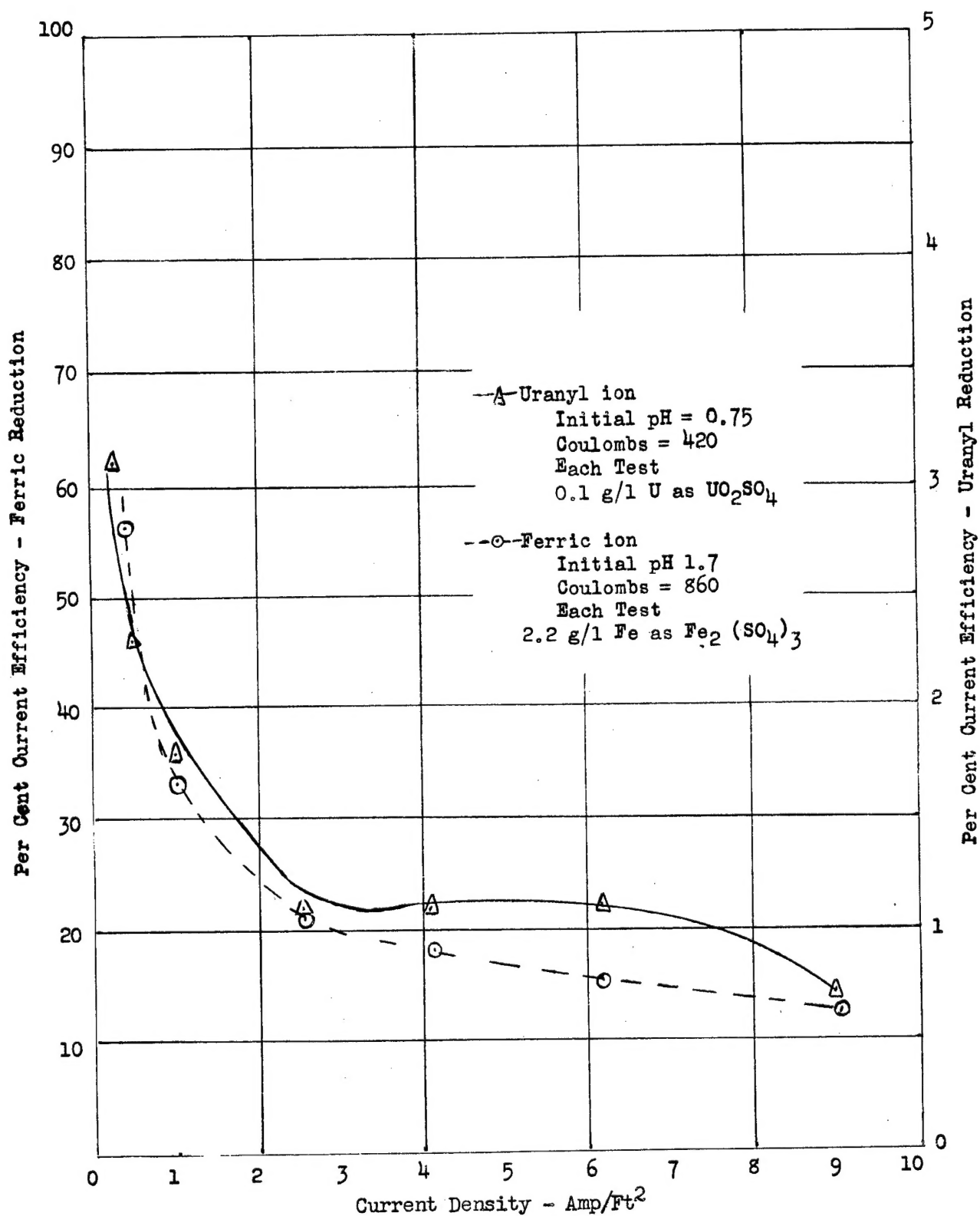Uranyl and Ferric Ions

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Figure 2.   Effect of Current Density on Current Efficiency for
Reduction of Ferric and Uranyl Ions

4. **Agitation.** The effect of mechanical agitation is shown in Table 2. Increasing agitation has a marked effect on the current efficiency, particularly at low-current densities. It should be noted that in most of the other tests described, hydrogen was evolved. Thus, some agitation was present in all tests.

Table 2. Efficiency of Reduction of Uranyl and Ferric Ions as a Function of Mechanical Agitation

Reduction Time Min.	Current Density Amp/sq ft	Agitation Speed RPM	Per Cent Current Efficiency
Uranyl Ion : Initial pH 0.75			
60	0.52	150	4.7
60	0.52	0	2.5
40	4.2	150	0.9
40	4.2	0	0.7
Ferric Ion : Initial pH 0.75			
60	1.04	500	100
60	1.04	0	40
30	4.2	500	44
30	4.2	150	35
30	4.2	0	21

5. **Time.** Figures 3 and 4 show the reduction and current efficiencies for ferric and uranyl ions as a function of time. Figure 4 shows a reduction of over 100 per cent for the uranyl ions. This is probably due to the formation of some U^{+3} ions in addition to the U^{+4} ions which were desired. As would be expected, the current efficiency decreases slowly with decreasing concentration of ferric or uranyl ion. The current efficiencies plotted in Figure 3 are the cumulative efficiencies. The actual efficiency at any one time is much less than that shown by the graph.

Figure 5 shows a semi-log plot of the per cent ferric ion remaining in solution as determined from the curves in Figure 3.

It is seen that both tests follow an exponential law quite closely. Therefore, the per cent reduction achieved in these solutions may be expressed as

$$\text{Per Cent Reduction} = 100 \, (1 - e^{-\lambda t}), \qquad (1)$$

where λ is a reduction rate constant and t is the reduction time; λ is calculated as 0.033 minute^{-1} for a current density of 1 ampere per square foot, and again as 0.011 minute^{-1} for a current density of 4.12 amperes per square foot. If these values are used in equation (1), t must be given in minutes.
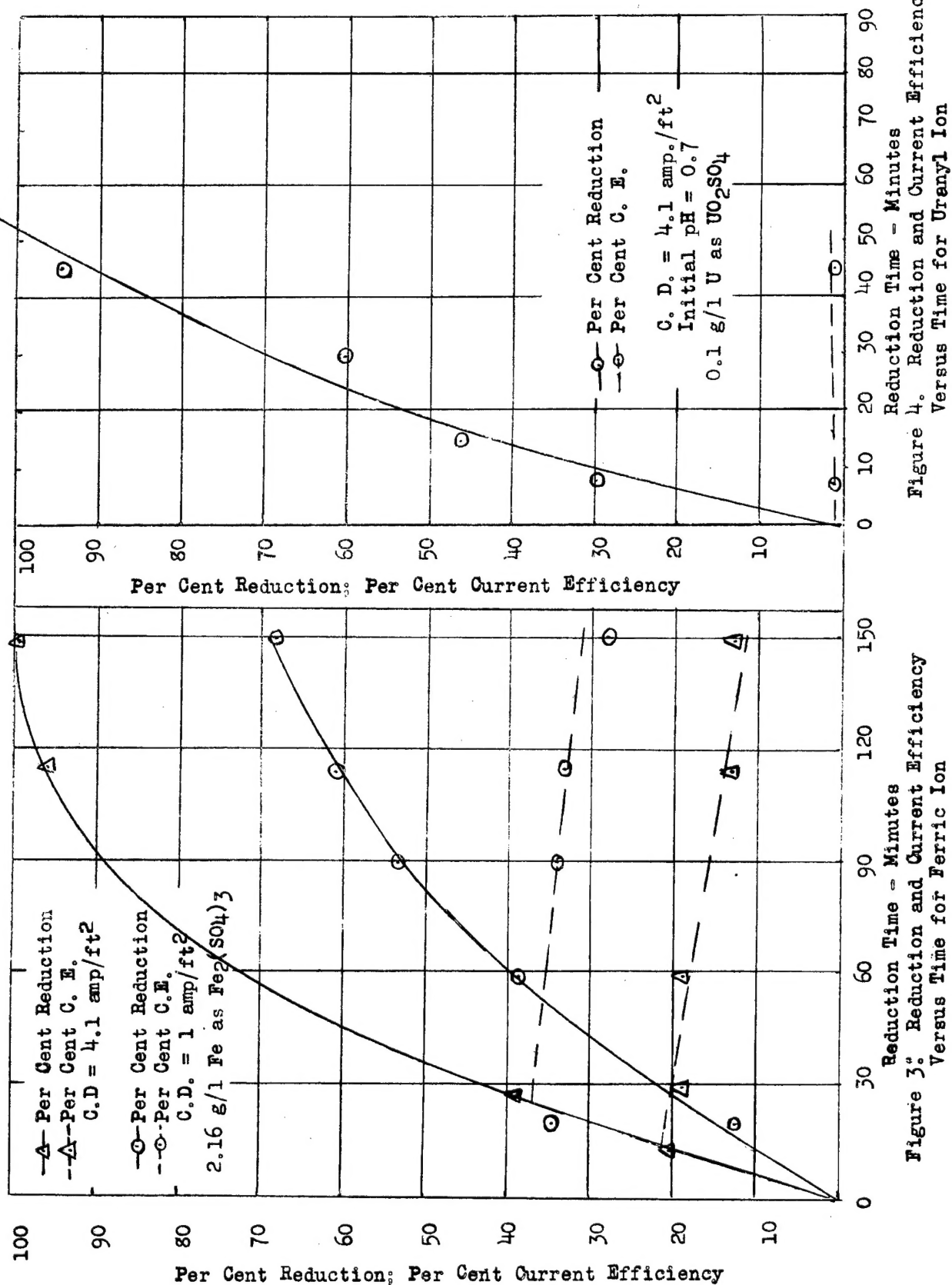
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Figure 4. Reduction and Current Efficiency
Versus Time for Uranyl Ion

Figure 3. Reduction and Current Efficiency
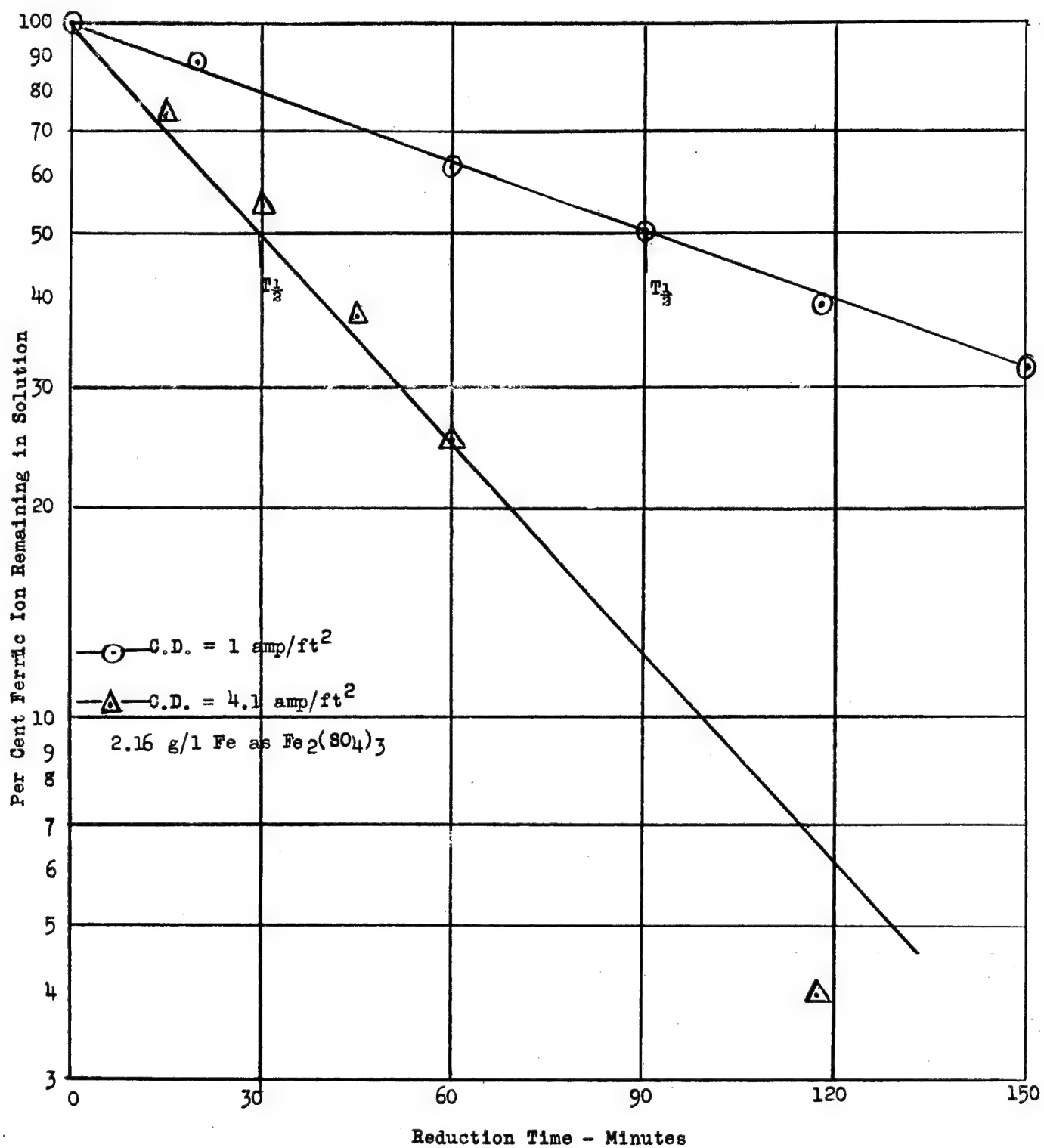Versus Time for Ferric Ion

Figure 5. Per Cent Ferric Remaining in Solution versus Reduction Time

The reduction of uranyl and ferric ions in the same solution was studied only as a function of the reduction time. The conditions of initial pH equal to 0.5 and low current density were chosen because they were found to be optimum in the tests already described. High current density was used to speed up reduction, although with some loss in efficiency. The results are shown in Figures 6 and 7. The current efficiencies plotted in Figures 6 and 7 are cumulative efficiencies. The actual efficiencies at any one time are much less than those shown by the graphs. The reduction of ferric ion is enhanced by the presence of uranyl ion as shown by the linearity of ferric reduction.

This may be due to any uranous ions formed at the cathode reacting with ferric ions in solution, giving efficiencies equal to stronger solutions.

In making up the reduction curves it was assumed that the uranium reduction did not start until the iron reduction was almost complete.
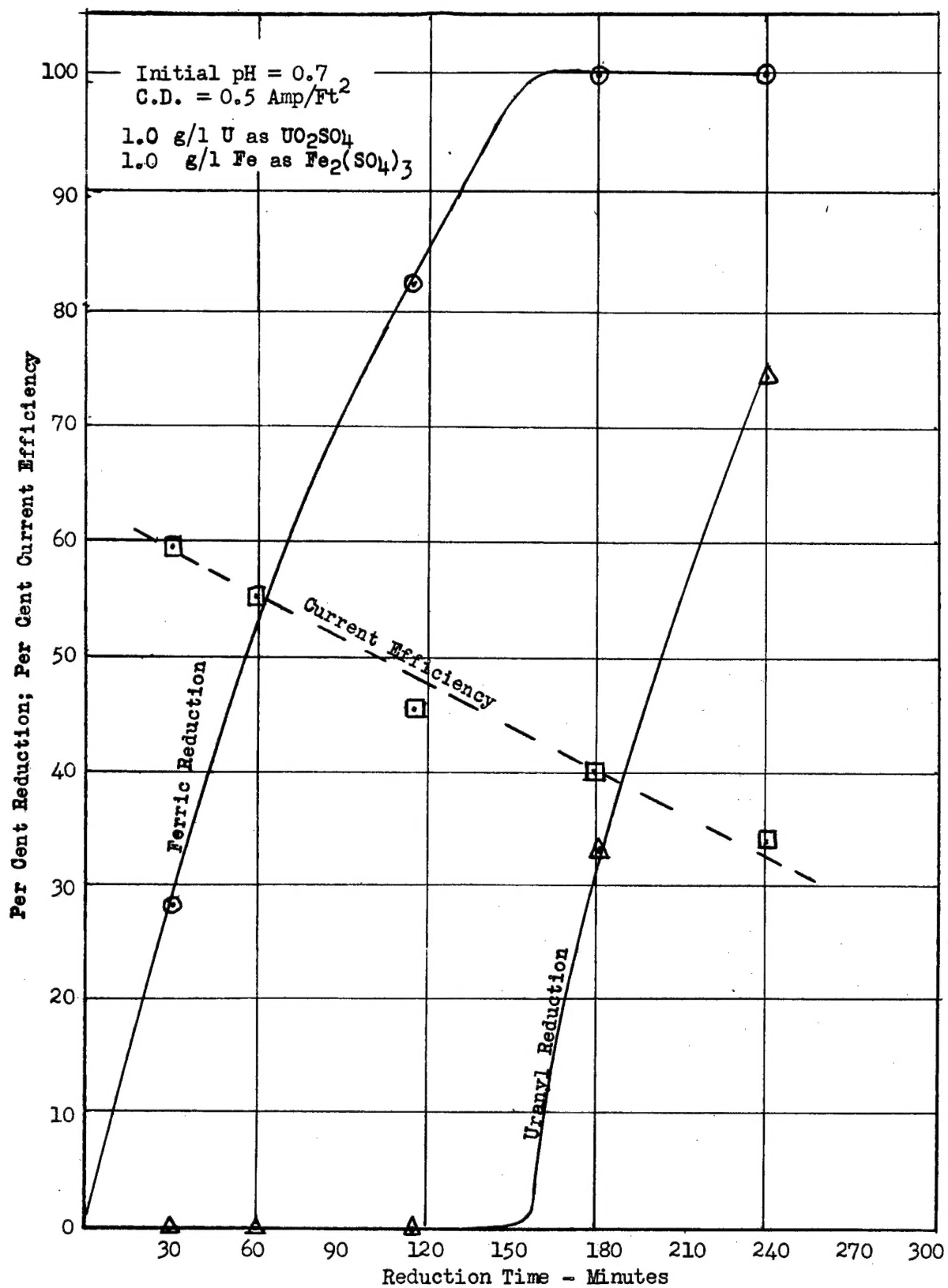
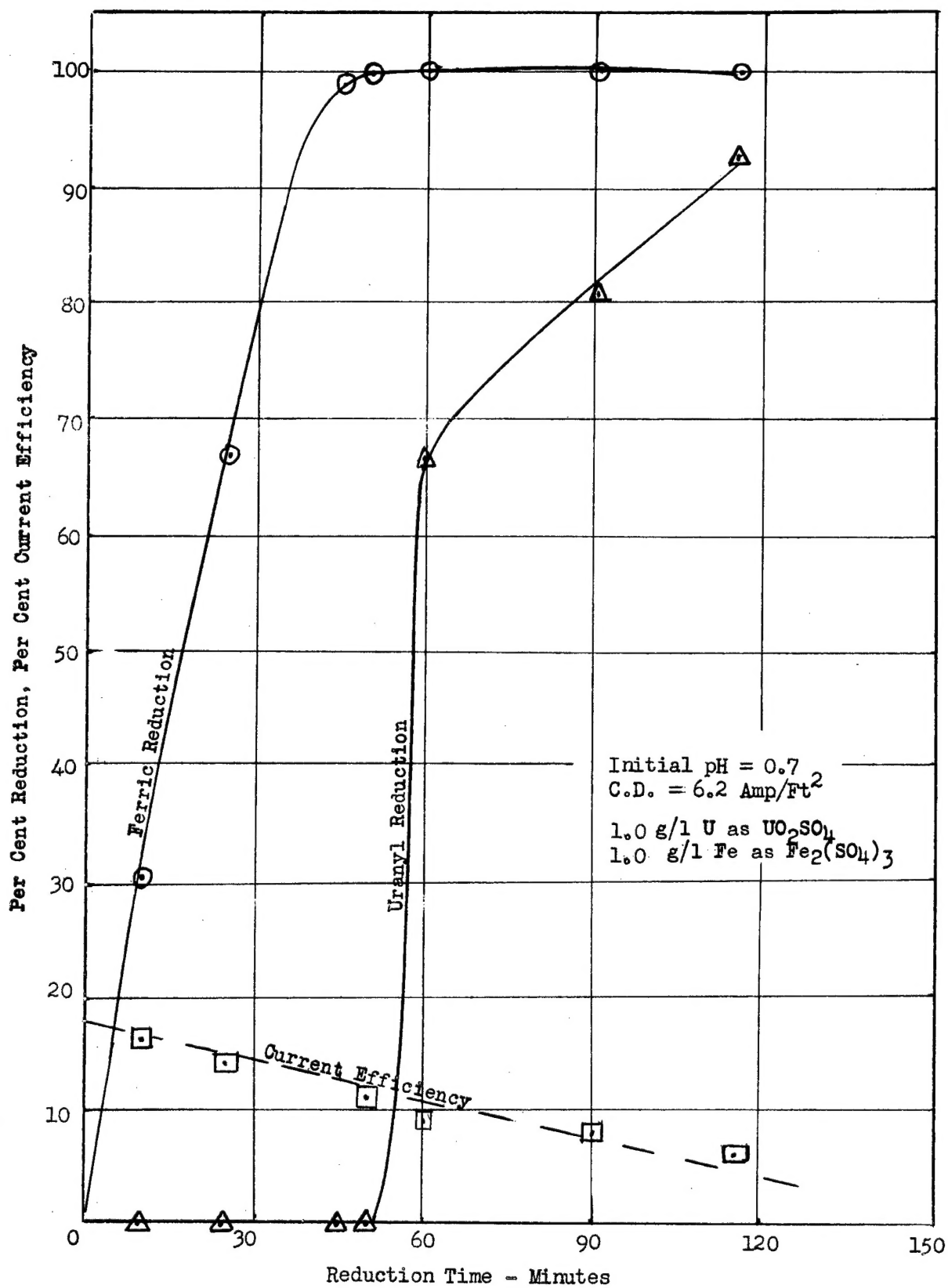Figure 6. Reduction of Ferric and Uranyl Solution vs. Time

Figure 7. Reduction of Ferric and Uranyl Solution versus Time

APPENDIX A

1. **Stock Solutions:**

   Ferric Sulfate Solution:

   100 g $Fe_2(SO_4)_3$ with about 6 H_2O, C.P., in 1 liter water.
   Chemical Analysis 21.6 g Fe^{+++} per liter. Diluted 10:1 for
   tests.

   Uranyl Sulfate Solution:

   17.7 g $2UO_2SO_4 \cdot 7H_2O$, C.P., in 1 liter water. Chemical Analysis
   9.75 g uranium per liter. Diluted 100:1 for tests.

2. **Titration Procedure:**

   $KMnO_4$ Solutions:

   One liter of 0.1 N $KMnO_4$ prepared from stock ampule. Diluted 10:1
   and standardized with sodium oxalate. Average value = 0.0098 N $KMnO_4$.

   Uranium Titration:

   Two 100 ml samples of catholyte titrated with 0.01 N $KMnO_4$ using 3
   drops Ferroin as indicator giving 0.4 ml blank.

   Ferric Titrations:

   Two 25 ml samples of catholyte titrated with 0.1 N $KMnO_4$ using 5 drops
   Ferroin as indicator giving 0.1 ml blank.

   Uranium and Ferric Titrations:

   Two 25 ml samples titrated with 0.01 N $KMnO_4$ using 3 drops Ferroin as
   indicator giving 0.4 ml blank.

   In these titrations it was assumed that all of the ferric ion would be
   reduced before any of the uranyl ion would be affected.